PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09D 11/00 — A1

(11) International Publication Number: **WO 99/54416**

(43) International Publication Date: 28 October 1999 (28.10.99)

(21) International Application Number: PCT/GB99/01217

(22) International Filing Date: 21 April 1999 (21.04.99)

(30) Priority Data:
9808480.9 21 April 1998 (21.04.98) GB

(71) Applicant *(for all designated States except US)*: COATES BROTHERS PLC [GB/GB]; Coates Lorilleux International, St. Mary Cray, Orpington, Kent BR5 3PP (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: CAIGER, Nigel, Antony [GB/GB]; 4 East Side, Hurst Batch, Wookey Hole, Wells, Somerset BA5 1BE (GB). SELMAN, Hartley, David [GB/GB]; Wayside Cottage, 562 Bath Road, Saltford, Bristol BS18 3JN (GB).

(74) Agent: WALDREN, Robin, Michael; Marks & Clerk, 57–60 Lincoln's Inn Fields, London WC2A 3LS (GB).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: RADIATION–CURABLE COMPOSITIONS

(57) Abstract

A vehicle for a hot melt ink–jet ink comprises at least 30 % by weight of a radiation curable material and a thickener. The vehicle is a thixotropic paste at 20 °C, preferably also at 25 °C and has viscosity of less than 25 centipoise, preferably 12 centipoise at at least one temperature in the range of from 40 °C to 130 °C. Another vehicle for a hot melt ink–jet ink comprises a radiation curable material. The curable material is a paste or a solid at 20 °C, preferably also at 25 °C and has a viscosity of less than 25 centipoise, preferably 12 centipoise at at least one temperature in the range of from 40 °C to 130 °C.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

RADIATION-CURABLE COMPOSITIONS

The present invention relates to radiation curable compositions suitable for use in the field of hot melt ink-jet printing and other applications.

Hot melt inks for use in ink-jet printing are compositions in which a dye or pigment is admixed with a vehicle which is essentially solid at room temperature but liquid at an elevated temperature at which print heads operate. The main advantage of hot melt inks over ink-jet inks which are liquids at room temperature, is that they solidify rapidly upon contact with the substrate. They are solid at room temperature and thus give a print quality which is essentially independent of the nature of the substrate. Moreover, independent temperature control of the substrate allows control of droplet spreading, again essentially independent of the properties of the substrate. This enables a superior print quality to be achieved than is obtainable with the liquid inks.

Current hot melt inks rely on solidification upon cooling to provide integrity of the print. Therefore, the durability of prints produced by the conventional kind of hot melt system is less than would be optionally desired in some applications.

Hot melt ink-like compositions are also used for modelling prototypes of articles of manufacture. A three-dimensional design produced on a computer aided design (CAD) system is used to control a hot-melt system which is used to "print" a hot melt composition in layers to build-up the complete prototype. The compositions used for this application need to be very hard at room temperature.

On the other hand, radiation-curable ink-jet inks are free-flowing liquids at room temperature. They spread rapidly on contact with the substrate until radiation curing causes "setting" of the ink droplets. As mentioned above, the print quality with such

inks is substrate dependent. It is difficult to control the degree of droplet spread and prevent inter-droplet smear.

JP 06200204 discloses a radiation curable ink for an ink jet printer which is solid at room temperature. It comprises from 10% to 30% by weight of a radiation-curable prepolymer and monomer and from 70% to 90% by weight of a wax and resin thickener.

New forms of hot melt ink formulation have now been devised which achieve benefits over both hot melt ink-type compositions and radiation curable ink-jet compositions.

Thus, in a first aspect, the present invention now provides a vehicle for a hot melt ink-jet ink, the vehicle comprising at least 30% by weight of a radiation curable material and a thickener, said vehicle being a thixotropic paste at 20°C, preferably also at 25°C and having a viscosity of less than 25 centipoise, preferably 12 centipoise at at least one temperature in the range of from 40°C to 130°C.

Vehicles according to the first aspect of the present invention are superior to those of JP 06200204 in that they have better flow properties within the printer apparatus and also have better curing properties.

However, a second aspect of the present invention provides a vehicle for a hot melt ink-jet ink, the vehicle comprising a radiation curable material, which curable material is a paste or solid at 20°C, preferably also at 25°C, the vehicle having a viscosity of less than 25 centipoise, preferably 12 centipoise at at least one temperature in the range from 40°C to 130°C.

Vehicles according to the second aspect of the present invention obviate the need for a separate thickener and in many embodiments, offer one or more other benefits in comparison with those materials disclosed in JP 06200204.

Those vehicles according to the second aspect of the present invention are solids (including waxy solids) and are analogues of conventional hot-melt compositions, except that they are radiation curable. Therefore, they exhibit higher durability than the former. Moreover, if they are printed onto a substrate supported on a heated plattern, the viscosity of the printed droplets can be reduced to a desired degree prior to cooling, to optimise print quality.

Vehicles according to the first aspect of the present invention (and those according to the second aspect of the present invention which are pastes at room temperature) may be characterised by their viscosity at 20°C, preferably 25°C.

Vehicles according to either aspect of the present invention which are pastes preferably have a viscosity of at least 500 centipoise (at a shear rate of 20 s^{-1}) at 20°C, preferably also at 25°C. The latter limit distinguishes the compositions from radiation-curable ink-jet compositions which are low viscosity liquids at room temperature. However, more preferably at 20°C (preferably also 25°C), vehicles according to the present invention have a viscosity of at least 800 centipoise, more preferably at least 1000 centipoise.

Vehicles according to the first aspect of the present invention are thixotropic pastes. Those according to the second aspect of the present invention are optionally pastes, in which case, they may or may not be thixotropic.

As used herein, any reference to a thixotropic (i.e. non-Newtonian) paste means that at a temperature of 20°C (preferably also at 25°C) and a shear rate of $20s^{-1}$, their viscosity is at least 500 centipoise (preferably at least 800 centipoise, more preferably at least 1000 centipoise) and at the same temperature at a shear rate of 1,000 s^{-1}, their viscosity is no more than 300 centipoise (preferably no more than 200 centipoise, more preferably no more than 150) centipoise. Moreover, after application of shear at a shear rate of 1,000 s^{1} centipoise for 60 seconds, the recovery time for recovery of the viscosity at $20s^{-1}$ to return to the same value or higher as originally measured at that shear rate is no more than 60 seconds, preferably no more than 5 seconds.

The compositions according to either aspect of the present invention need to be liquid and jettable (i.e. having a viscosity of less than 25 centipoise, preferably 12 centipoise), at the print head temperature, i.e. somewhere in the range of from 40°C to 130°C.

Any vehicle according to either aspect of the present invention may consist of a single radiation-curable material, or a combination of materials, any or all of which is radiation-curable.

Vehicles according to the first aspect of the invention must include a thickener. Preferably the thickener used according to the first aspect of the invention is not radiation curable. In the case of the second aspect of the present invention, the radiation curable material is sufficiently viscous to endow the vehicle with the necessary solidity or paste-like viscosity at 20°C, preferably 25°C. However, optionally, an auxiliary thickener (which may be a single component or combination of components) may also be included. If a thickener is used according to the second aspect of the invention such thickener is preferably not radiation curable.

In the case of the vehicles according to the first aspect of the present invention, the amount of the radiation curable material is preferably from 35% to 98%, more preferably from 50% to 95%, still more preferably from 60% to 92% by weight of the vehicle. The thickener preferably constitutes from 0.5% to 30%, more preferably from 3% to 10% by weight of the vehicle.

In the case of vehicles according to the second aspect of the present invention, the amount of the radiation curable material is preferably from 5% to 50% by weight of the vehicle. The thickener then preferably constitutes from 0.1% to 10%, more preferably from 1% to 5% by weight of the vehicle.

In the case of vehicles according to the second aspect of the present invention, an auxiliary thickener may optionally be included. An auxiliary radiation curable component may also be included which may or may not meet the viscosity requirement

of the main radiation curable material, as desired. In other words, this auxiliary radiation curable material may in itself be radiation curable and/or at least capable of involvement in curing of the main radiation curable material (e.g. by acting as a cross-linking agent).

Materials suitable for use as radiation curable materials in the first aspect of the invention or auxiliary radiation curable components in the second aspect of the invention fall into two categories.

The first category comprises those materials which are curable (i.e. at least capable of involvement in a curing reaction) in the presence of a free radical initiator. The second category comprises those which are curable in the presence of a cationic initiator. The second category is mainly applicable to the first aspect of the present invention.

The amount of photoinitiator will normally be from 1%, to 15%, preferably from 1% to 10% by weight of the total composition. A wide spectrum of photoinitiators is commercially available and a non-exhaustive selection of appropriate types include xanthone or thioxanthone types, benzophenone types, quinone types and phosphine oxide types. Sometimes, it is also desirable to include a co-initiator, as well as a primary photoinitiator, most preferably of the amine or aminobenzoate type. In that case, it is preferred for the total photoinitiator (primary initiator plus co-initiator) to be within the aforementioned preferred range. For example, typical co-initiators are aminobenzoate and acrylated amine co-initiators, these generally being used with the xanthone/thioxanthone types of primary photoinitiator. Suitable photoinitiator stabilisers include those disclosed in EP-A-0 465 039.

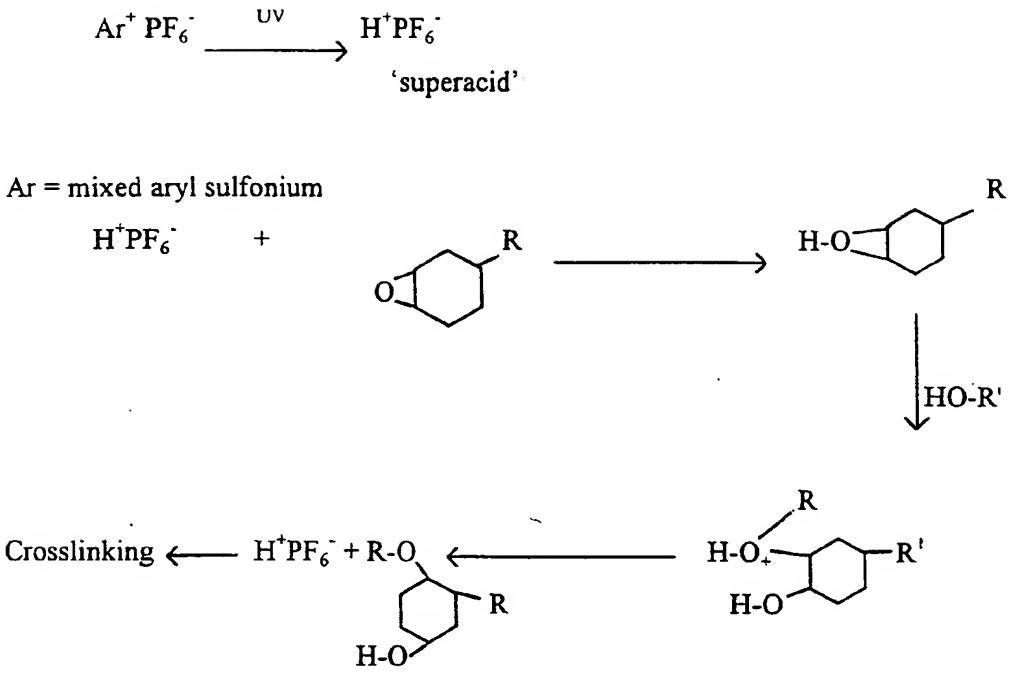
The first category (free radical polymerisable) of materials generally comprises monomers and oligomers having a degree of ethylenic unsaturation, e.g. the (meth) acrylates but preferably they comprise materials having difunctional unsaturated moieties (e.g. vinyl groups) or else have mono-functional unsaturation and must be used

in conjunction with separate cross-linking agents in order to allow polymerisation upon curing.

One class of suitable difunctional materials are difunctional acrylates (e.g. difunctional diacrylates) such as a difunctional cycloaliphatic acrylate, for example a difunctional cyclohexane acrylate. A specific material of the latter kind is cyclohexane dimethanol diacrylate sold as CD406X ex Sartomer.

One class of monofunctional materials which are radiation curable and may be used in the presence of a cross-linking agent comprise a monofunctional acrylate such as an acrylate ester of a fatty alcohol or of an ethoxylated fatty alcohol. These are especially (although not exclusively) useful as radiation curable materials for vehicles according to the second aspect of the present invention. Suitable examples of such materials are the acrylate esters of Unilin (Trademark) alcohols and of the Unithox (Trademark) ethoxylates ex Petrolite Corp.

Alternatively, cationic curing materials of the second class could be used in place of or together with (so called "hybrid systems") the above mentioned materials of the first class. In these systems crosslinking takes place by an ionic rather than free radical mechanism. One common chemistry used is that of the cycloaliphatic epoxides which cure in the presence of strong cationic initiators. Onium salt photoinitiators are commonly used which undergo photolysis in the presence of uv light to form highly efficient cationic species. A general scheme might be:



Where a radiation curable material (either as primary curable material or as all or part of the thickener) needs the presence of a cross-linking agent to make it sufficiently curable, such cross-linking agent may for example be selected from multifunctional acrylates (for free radical curing systems) and multifunctional epoxides and/or polyols (for cationic curing systems).

Radiation curing, in the context of the present invention means a polymerisation reaction effected by application of any suitable radiation such as electron beam radiation or any appropriate electromagnetic radiation such as in the ultraviolet (UV) spectrum. However, many radiation curable components require the presence of a photoinitiator.

Many suitable materials which are not radiation-curable and may be used as (non-curable) thickeners in the first aspect of the present invention or auxiliary thickeners in the second aspect of the invention are polymeric substances which are hard at room

temperature but which become liquid at elevated temperatures. Such materials are preferably also film-forming polymers at room temperature, e.g. styrene polymers or copolymers, hydrocarbon resins, phenolic resins and fatty acid amides.

Other materials usable as non-curable thickeners are the urethane oligomers described in PCT Patent Specification No. WO 94/14902. These oligomers are the reaction products of diisocyanates with a monohydric alcohol component, optionally followed by another monohydric component or a dihydric alcohol component followed by a monohydric alcohol component. Another class of suitable such material comprises the urethane- and urea-amides disclosed in our unpublished UK patent application no. 9519646.5. These materials are the reaction products of a mono- or di-isocyanate with one or more functional amides. They typically have molecular weights in the range from 800-1400.

Yet other materials which may typically be used as non-curable thickeners are waxes, typical examples being stearone, carnauba wax, stearyl stearamide, hydrogenated castor oil, erucamide, acid waxes (e.g. Wax S ex Hoechst), ester waxes (e.g. Wax E ex Hoechst, Syncrowax ERLC C_{18}-C_{36} ester glycol esters, Syncrowax HGLC C_{18}-C_{36} acid triglyceride ex Croda).

When used in an ink-jet ink, generally the vehicle as a whole will make up 50-98% by weight, especially 75-95% by weight of the composition, optionally with one or more optional additives for example, antioxidants, surfactants, levelling additives, photoinitiator stabilisers, wetting agents and pigment stabilisers.

Suitable surfactants are preferably of non-ionic type, for example Fluorad FC430 (ex 3M Corp.). Such surfactants (when present) are preferably included in an amount of from 0.1% to 10% by weight of the total composition.

Hot melt inks can basically be considered to consist of the vehicle plus a colourant optionally with any minor ingredients such as hereinbefore described. The present invention extends to compositions according to the present invention which function as hot melt ink vehicles and those which comprise such a composition according to the present invention together with a colourant, or else otherwise coloured as described hereinbelow.

Broadly speaking, colourants may be considered as falling into two classes, namely dyes, which are substantially soluble in the ink composition, and pigments, which are dispersed in the ink composition in the form of fine particles, if necessary with the aid of a suitable dispersant. The term "colourant" includes materials which endow a non-visible optical property (e.g. fluorescence) to the ink.

Where dyes are employed, these may be selected from a wide range of classes, so long as they are soluble in the ink vehicle. A non-exhaustive list of dyes includes those of the Orasol range ex CIBA and the Savinyl range ex Hoechst. Respectively, typical examples are Orasol blue GN, Yellow 4GN; Savinyl Black RLS and Red GLS.

Pigments may be selected from a wide range of classes, for example, Pigment Red 57:1, Pigment Red 52:2, Pigment Red 48:2, Pigment Blue 15:3, Pigment Green 7, Pigment Yellow 83, Pigment Yellow 13, Pigment White 6, Pigment Black 7. A non-exhaustive list of examples of such pigments include the following from the Irgalite range ex CIBA: Rubine L4, Bordeaux CM, Red 2BP, Blue LG, Green GLN, Yellow B3R and yellow LBG; as well as Tioxide RHD6 (ex Tioxide) and Special Black 250 (ex Degussa).

Where the colourant is a pigment, then unless the pigment is self-dispersing, it is necessary to incorporate a dispersant therefor. Suitable dispersants typically include polyester, polyurethane or polyacrylate types, especially in the form of high molecular weight block co-polymers, and would typically be incorporated at from 2.5% to 150%

by weight of the pigment. Suitable examples are Disperbyk 161 or 162 (ex BYK Chemie) or Solsperse ex Zeneca.

Another way of introducing a colour (or other optical property) is to incorporate an ingredient which itself endows the property, e.g. a polymer or oligomer having a dye moiety bonded onto or incorporated therein. Suitable materials are disclosed in GB-A-2 038 849, US-A-5 264 507, US-1-5 098 475, EP-A- 540 248 and our unpublished UK patent application no. 9520470.7.

Preferably the vehicles according to either, or both, of the first and second aspect comprise one or more radiation curable materials which are coloured.

The present invention will now be explained in more detail by way of the following description of non-limiting examples.

	Example	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
	Form	Solid	Solid	Paste	Paste	Paste	Paste	Paste	Paste
	Viscosity@ 25°C($20s^{-1}$)	Solid	Solid	1000cps	1100cps	1400cps	1300cps	1200cps	1000cps
	Visosity @ 25°C($1000s^{-1}$)	Solid	Solid	~110cps	190cps	~120cps	~120cps	~110cps	~110cps
	Viscosity @ 90°C ($1000s^{-1}$)	5.2	5.8	4.1	14cps	4.0	13.0	17.0	15.0
Formulation									
Acrylate ester of Unilin 425 Alcohol wax X 8505 (1)		21.0	40.0	5.0	5.0	-	-	-	-
Unilin 350 (1)						6.0	-	2.0	3.0
Syncrowax ERLC (4)							5.5	3.0	3.0
Cyclohexane dimethanol diacrylate		-	44.8	-	-	-	-	-	-
Dipenta erythritol Pentaacrylate (2) SR 399		-	-	-	10.0	-	-	-	5.0
Ethoxylated neopentyl glycol diacrylate		64.2	-	79.8	64.3	85.6	-	30.0	-
Isobornyl acrylate		-	-	-	-	-	21.0	10.0	30.0

	Example	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
	Form	Solid	Solid	Paste	Paste	Paste	Paste	Paste	Paste
Formulation									
Ethoxylated trimethylopropane triacrylate		-	-	-	-	1.5	38.2	37.3	24.0
1,4 butanedrol diacrylate		-	-	-	-	-	20.3	-	20.0
Acrylate Amine CN384 (2)		-	-	-	-	-	5.0	5.0	-
Isopropyl thioxanthone		2.1	2.5	2.5	7.5	1.7	1.5	2.5	1.8
4-phenyl benzophenone		1.0	1.0	1.0	3.0	2.0	1.5	1.0	2.0
2-benzyl-2-dimethylamine-1-(4-morpholinophenyl) butan-1-one		1.0	1.0	1.0	3.0	1.0	0.8	1.0	1.0
(2-ethyl)hexyl 4-dimethylamino benzoate		3.0	3.0	3.0	-	2.0	-	-	2.0
Fluorosurfactant (Fluorad FC430(3)		0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Carbon black Pigment/Dispersant		7.5	7.5	7.5	7.0	-	-	-	-

	Example	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
	Form	Solid	Solid	Paste	Paste	Paste	Paste	Paste	Paste
Pigment Blue 15:3/Dispersant		-	-	-	-	-	6.0	-	-
Pigment Red 122/Dispersant		-	-	-	-	-	-	8.0	8.0

Total 100%

(1) = ex Petrolite Corporation

(2) = ex Sartomer

(3) = ex 3M

(4) = ex Croda

Example	9	10
Form	Paste	Paste
Viscosity @ 25°C ($20s^{-1}$)	~3200 cps	~3900 cps
Viscosity @ 25°C ($1000s^{-1}$)	~130 cps	~160 cps
Viscosity @ 80°C ($1000s^{-1}$)	~16.3 cps	~14.0 cps
CYRACURE UVR 6105 (1) (3,4, Epoxy cyclohexyl methyl-3,4-epoxy cyclohexane carboxylate)	78.8	73.8
CYRACURE UV1 6900 (1) (Mixed triaryl sulfonium Hexafluorophosphate salt)	6.0	6.0
Rapicure HBVE (4-hydroxybutyl vinyl ether)	10.0	15.0
Hoechst Wax E (2)	5.0	-
Unilin 425 (3)	-	5.0
Fluorosurfactant (Fluorad FC 430) (4)	0.2	0.2
Total %=	**100**	**100**

(1) ex Union Carbide

(2) ex Hoechst

(3) ex Petrolite

(4) ex 3M

In the light of this disclosure, modification of the described examples, as well as other examples, all within the scope of the present invention as defined by the appended claims will now become apparent to persons skilled in the art.

CLAIMS:

1. A vehicle for a hot melt ink-jet ink, the vehicle comprising at least 30% by weight of a radiation curable material and a thickener, said vehicle being a thixotropic paste at 20°C, preferably also at 25°C, said vehicle having a viscosity of less than 25 centipoise, preferably 12 centipoise at at least one temperature in the range of from 40°C to 130°C.

2. A vehicle according to claim 1, wherein the thickener is not radiation curable.

3. A vehicle according to claim 1 or claim 2, wherein the thickener is present at from 0.5% to 30%, preferably from 2% to 10% by weight of the vehicle.

4. A vehicle according to any preceding claim, comprising from 35% to 98%, preferably from 50% to 95%, most preferably from 60% to 92% by weight of the radiation curable material.

5. A vehicle according to any preceding claim, wherein the radiation curable material is curable by a free radical initiator.

6. A vehicle according to claim 5, wherein the radiation curable material comprises at least one ethylenically unsaturated monomer or oligomer, preferably a (meth) acrylate monomer or oligomer.

7. A vehicle according to claim 5 or claim 6, wherein the radiation curable material comprises a monofunctional acrylate.

8. A vehicle according to claim 7, which further comprises a cross-linking agent.

9. A vehicle according to claim 5 or claim 6, wherein the radiation curable material comprises a difunctional acrylate.

10. A vehicle according to claim 9, wherein the difunctional acrylate is a difunctional cycloaliphatic acrylate.

11. A vehicle according to any of claims 5-10, further comprising a photoinitiator.

12. A vehicle according to any of claims 1-3, wherein the radiation curable material is curable in the presence of a cationic initiator.

13. A vehicle according to claim 13, further comprising a cationic initiator.

14. A hot melt ink comprising a vehicle according to any preceding claim and a colourant.

15. A hot melt ink comprising a vehicle according to any one of claims 1-13which vehicle comprises one or more radiation curable materials which are coloured.

16. A vehicle for a hot melt ink-jet ink, the vehicle comprising a radiation curable material, which curable material is a paste or a solid at 20°C, preferably also at 25°C, and having a viscosity of less than 25 centipoise, preferably 12 centipoise at at least one temperature in the range of from 40°C to 130°C.

17. A vehicle according to claim 16, further comprising an auxiliary thickener.

18. A vehicle according to claim 17, wherein the auxiliary thickener is not radiation curable.

19. A vehicle according to claim 18, wherein the auxiliary thickener is present at from 0.1% to 10%, preferably from 1% to 5% by weight of the vehicle.

20. A vehicle according to any of claims 16-19 further comprising an auxiliary radiation curable component.

21. A vehicle according to claim 20, wherein the radiation curable material and/or the auxiliary radiation component is curable by a free radical initiator.

22. A vehicle according to claim 20 for claim 21, wherein the auxiliary radiation curable component is curable by a cationic initiator.

23. A vehicle according to any of claims 16-22, comprising from 5% to 50% by weight of the radiation curable material.

24. A vehicle according to claim 21, wherein the radiation curable material comprises a monofunctional acrylate.

25. A vehicle according to claim 24, wherein the monofunctional acrylate is an acrylate ester of a fatty alcohol or of an ethoxylated fatty alcohol.

26. A vehicle according to claim 24 or claim 25, which composition further comprises a cross-linking agent.

27. A vehicle according to any one of claims 16 to 26, further comprising a photoinitiator.

28. A hot melt ink comprising a vehicle according to any one of claims 16-27 and a colourant.

29. A hot melt ink comprising a vehicle according to any of claims 16-28, which vehicle comprises one or more radiation curable materials which are coloured.

INTERNATIONAL SEARCH REPORT

Int Jonal Application No
PCT/GB 99/01217

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 337 705 A (SERICOL GROUP LTD) 18 October 1989 (1989-10-18) page 2, line 21-55 ---	1,2,5-8, 11,14,16
A	WO 96 28305 A (MARKEM CORP) 19 September 1996 (1996-09-19) page 3, line 14-21 page 4, line 20-27 ---	16
A	EP 0 204 575 A (MITSUBISHI RAYON CO) 10 December 1986 (1986-12-10) --- -/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 July 1999	28/07/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Miller, A

3

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Int Ional Application No
PCT/GB 99/01217

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropnate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9433 Derwent Publications Ltd., London, GB; Class A97, AN 94-269649 XP002109160 & JP 06 200204 A (BROTHER KOGYO KK), 19 July 1994 (1994-07-19) cited in the application abstract	1

3

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int Jonal Application No
PCT/GB 99/01217

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0337705 A	18-10-1989	GB 2217338 A	25-10-1989
WO 9628305 A	19-09-1996	EP 0814961 A	07-01-1998
		JP 11501877 T	16-02-1999
		US 5700313 A	23-12-1997
EP 0204575 A	10-12-1986	JP 1049430 B	24-10-1989
		JP 1564736 C	12-06-1990
		JP 61278577 A	09-12-1986
		US 4680368 A	14-07-1987
JP 6200204 A	19-07-1994	NONE	